A SURVEY OF THE LITERATURE ON THE ELECTRODEPOSITION OF MOLYBDENUM

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SUMMARY

A survey of the literature was made covering the use of aqueous nonaqueous, and fused-salt systems for the electrowinning or electroplating of molybdenum metal.

The survey was prepared in order to provide background for further investigations directed toward the electrodeposition of pure molybdenum metal from either aqueous or nonaqueous mediums. While a thorough effort was made to cover all available references, a critical review was not attempted nor does this survey pretend to be exhaustive in nature.

INTRODUCTION

Molybdenum, because its atom in various compounds exists in 5 different oxidation states, +2, +3, +4, +5, and +6, presents a difficult problem for the electrochemist. The problem is further complicated by the tendency of molybdate ions to form polyions by polymerization and condensation reactions, which depend upon pH and concentration. In any given solvent system, molybdenum compounds may disproportionate to give complex compounds in which the metal ion may exist in several of its different oxidation states. This is especially true when molybdenum solutions are subjected to the passage of an electric current. In the light of these facts, it is probable that only complex systems will result from efforts to electrodeposit the metal from any particular medium.[3/] The self-polarizing tendency of molybdenum further complicates the problem, as does its tendency to form inner orbital complexes. Frequent claims for the electrodeposition of molybdenum from aqueous, nonaqueous, and fused-salt electrolytes are reported in the literature; however, most of the claims for deposition of the metal do not appear valid, and efforts to duplicate much of this work at the Northwest Electrodevelopment Experiment Station were unsuccessful. Lower oxides or codeposits of molybdenum with iron, lead, or platinum were effected. In a few instances, thin metallic blushes were obtained, after which deposition ceased and only lower oxides continued to deposit.

DEPOSITION FROM AQUEOUS SOLUTIONS

J. Feree[4/] reported that a 4.8 percent molybdenum mercury amalgam is formed upon electrolysis of a saturated solution of molybdenum trioxide

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3/ Killeffer, D. H., and Linz, Arthur, Molybdenum Compounds, Interscience Publishers, Inc., New York, 1952, 407 pp.

4/ Feree, J., On the Amalgams of Molybdenum and Some Properties of Molybdenum Metal: Comp. rend., vol. 22, 1896, p. 753.

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in 22° Baume hydrochloric acid, utilizing a mercury cathode and a platinum anode at a current density of 5 amps./sq. cm. The amalgam can be enriched to 24 percent molybdenum content by pressing between filter paper. The metal obtained by a low vacuum distillation of the amalgam is a black, finely divided, pyrophoric powder.

Electrodesposition of molybdenum at a mercury cathode from a 1.20-1.40 N. sulfuric acid electrolyte containing sodium molybdate (0.15 gm. MoO_3/liter is reported by Merill and Russell.[5/] Best results were obtained at a current density ranging from 0.6 - 1.0 amps. sq. cm., under which conditions 0.1 gram of molybdenum was deposited in 1 hour. Temperatures ranged from 35° C. at low current densities to 90° C. at the higher current densities.

C. J. Fink and C. H. Eldridge[6/] claim that molybdenum may be deposited from an acid bath containing molybdic acid and an excess of boric acid. Only thin plates are obtained.

R. E. Meyers[7/] using an electrolyte composed of sodium molybdate or molybdenum trioxide acidified with sulfuric acid, obtained quantitative yields of molybdenum as a brilliant white amalgam with a mercury cathode. Electrolysis was carried out at 5.5 volts and a cathode current density of from 0.2 - 0.3 amps./sq. cm. over a period of 25 hours.

H. Krause,[8/] in a review, states that molybdenum is deposited from a solution containing 10 grams of ammonium molybdate and 10-20 grams of ammonium nitrate in 1 liter of water. The metal is recovered as a fine black powder at a current density of 0.2 - 0,3 amps./sq. cm. and about 2 volts.

K. A. Paul[9/] describes conditions whereby molybdenum may be electroplated from a solution of molybdenum oxides in halogen acids of specific gravity 1.2-1.3. These solutions are diluted with water to 10-25° Baume and plating is effected at a current density of 75 amps./sq. in. and up to 6 volts.

W. P. Price and O. W. Brown[10/] claim that smooth steel-gray deposits of molybdenum may be obtained from an electrolyte composed of 60 grams of

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5/ Merill, J. L., and Russell, A. S., The Electrolytic Deposition of Molybdenum at a Mercury Cathode: Jour. Chem. Soc., 1929, p. 2387.

6/ Fink, C. G., and Eldridge, C. H., Electrodeposition of Molybdenum: Canadian Patent 274,429, Oct. 4, 1927.

7/ Meyers, R. E., Electrochemical Analysis: Jour. Am. Chem. Soc. vol. 26, 1904, p. 1124.

8/ Krause, H., New Electrolytic Deposits: Feinmech. u. Präzision, vol. 41, 1933, p. 106.

9/ Paul, K. A., Russian Patent 53,756, Aug. 31, 1938.

10/ Price, W. P., and Brown, O. W., The Electrodeposition of Molybdenum From Aqueous Solutions: Trans. Am. Electrochem. Soc., vol. 70, 1936, p. 473.

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molybdenum trioxide in 150 cc. of sulfuric acid of 1.450 specific gravity. Platinum was used for both the anode and the cathode during the reducing period of the run, which was carried out for 240 ampere-hours at a cathode current density of 2.0 - 2.5 amps./sq. dm. Electrodeposition was carried out utilizing platinum or lead anodes and a copper cathode at a current density of 36 amps./sq. dm. and a temperature of -50° - 55° C.

A. S. Minin[11] claims that molybdenum may be electroplated from a solution of ammonium molybdate, ammonium hydroxide, and ammonium sulfide at temperatures ranging from 60° - 70° C.

Ksycki and Yntema[12 13 14] state that metallic molybdenum can be deposited from aqueous solutions of molybdic acids containing high concentrations of such salts as formates, acetates, propionates, fluorides, and phosphates of sodium, potassium, and ammonium. Close control of pH within a definite range is necessary to obtain bright plate. The current density can be varied from 0.06 - 3.3 amps./sq. cm. and the temperature from 30° - 55° C. It is claimed that deposits were obtained on copper, nickel, and iron cathodes, platimum or carbon serving as the anode.

L. F. Yntema[15] reports that molybdenum may be deposited from an acid solution. Two grams of molybdic acid are evaporated down to dryness in 15 cc. of 34-percent hydrobromic acid and the dark-brown residue dissolved in 6 cc. of 2.5 molar dipotassium citrate and then diluted to 20 cc. This solution is then neutralized with KOH and 1 cc. of 2.5 molar citric acid added. Deposition proceeded at a current density of 9-12 amps./sq. dm.

FUSED SALT ELECTROLYSIS

One of the earliest means of depositing molybdenum metal from a fused salt bath is the method of Gustave Gin[16] who utilized a double chloride of sodium molybdenum hexachloride ($NaMoCl_6$). Porous deposits were obtained at a carbon cathode with a current density of 1 amp./sq. cm. and 6 - 7 volts. He also reported that molybdenum may be deposited on an iron cathode from a bath containing the double fluoride of calcium and molybdenum. Gin recommends the use of a molten lead cathode in conjunction with the double chloride, the lead is subsequently distilled away from the molybdenum. A similar process is referred to in publications by Gmelin[17] and by Althertum.[18]

11/ Minin, A. S., Russian Patent 49,863, 1941; C. A. vol. 39, 1945, p. 873.
12/ Ksycki, M. J., and Yntema, L. F., The Electrodeposition of Molybdenum From Aqueous Solutions: Jour. Electrochem. Soc. vol. 96, 1949, p. 48.
13/ Yntema, L. F., and Ksycki, M. J., Process for Electroplating Molybdenum and Molybdenum Alloys: United States Patent 2,499,808; 1950.
14/ Yntema, L. F., and Ksycki, M. J., Process for Electroplating Molybdenum and its Alloys: United States Patent 3,499,807; 1950.
15/ Yntema, L. F., Electrodeposition of Chromium, Molybdenum, and Tungsten: Jour. Am. Chem. Soc., vol. 54, 1932, p. 3775.
16/ Gin, G., Electrometallurgy of Rare Metals: Trans. Am. Elec. Soc., vol. 12, 1907, p. 411.
17/ Gmelin, Leopold, Hanbuch der anorg. chemie.: Syst. 53, Molybdan; 8th ed., 1935, pp. 35-155.
18/ Althertum, H. Ztschr. anorg. Chem., vol. 42, 1929, p. 4.

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Beckman[19 20] claims that molybdenum may be deposited from a fused salt bath obtained by heating molybdenum trioxide with calcium oxide in an electric furnace to form a double salt of the metal. Additional oxide is added to the fused salt, which is then subjected to electrolysis at temperatures ranging from 960° - 1,400° C.

Electrolysis of a fused salt bath composed of equimolar proportions of molybdenum pentachloride, aluminum chloride, and sodium chloride at 200° C. yields molybdenum, according to Forland.[21]

The use of anhydrous molybdenum salts in conjunction with salts of electropositive metals such as the chlorides of barium or calcium is reported by Kratky and Bruckner[22] to yield massive metal upon electrolysis.

Andrieux[23 24] reports that tungsten and molybdenum may be prepared by electrolysis of their oxides in a molten bath of boron sesquioxide (B_2O_3) or borates to which fluorides or other salts that lower the melting point have been added. Zinc oxide was utilized in conjunction with molybdenum oxide and a fluoride in one bath to deposit molybdenum. A similar bath composed of boron compounds, sulfates, bisulfates, silicates, or cyanides along with molybdenum oxide is patented by Siemens and Halske.[25] The electrolysis at elevated temperatures of molybdic acid in fused HPO_3 and $NaPO_3$ and mixtures of $NaPO_3$ and $Na_2P_2O_7$ with a P_2O_5 to Na_2O ratio of less than 1 is reported to yield molybdenum in the form of fine white needles according to Hartman and Conrad.[26]

L. R. Föörland[27] claims that molybdenum can be manufactured by electrolyzing molten mixtures of salts that, in addition to molybdenum chlorides, contain conducting salts of metals that have a greater affinity for chlorine than does molybdenum.

Tumanov[28] reports that molybdenum may be electrodeposited from a solution of molybdenum oxide in fused cryolite.

19/ Beckman, J. W., United States Patent 973,336, 1910.
20/ Beckman, J. W., Trans. Am. Elec. Soc., vol. 19, 1911, p. 171.
21/ Forland, T. R., Molybdenum: United States Patent 1,305,350, June 3, 1919.
22/ Kratky, A., and Bruckner, W., German Patent 263,301, 1911.
23/ Andrieux, L., An Ingenious Method for the Electrolysis of Oxides, Applications to the Preparation of Certain Metals and Borides: Compt. rend. vol. 184, 1927, p. 91.
24/ Andrieux, L., Researches on the Electrolysis of Metallic Oxides Dissolved in Fused B_2O_3 or Fused Borates: Masson et Cie, PhD. Thesis, University of Paris, 1929.
25/ Siemens, E. W., and Halske, A. G., Electrodeposition of Metals: British Patent 286,457, Mar. 8, 1927.
26/ Hartman, H. E., and Conrad, U., Electrolysis in Phosphate Melts: Ztschr. anorg. Chem., vol. 233, 1937, p. 313.
27/ Föörland, L. R., Metallic Molybdenum: Norwegian Patent 30,305, Jan. 12, 1920.
28/ Tumanov, N. N., Electrodeposition of Molybdenum: Russian Patent 53,257, May 31, 1938.

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The most recent paper dealing with the electrodeposition of molybdenum metal is that of Brenner and Senderoff,[29] who successfully deposited molybdenum from a fused bath composed of potassium hexachlormolybdate (K_3MoCl_6) in a 1 to 1 mixture of sodium and potassium chloride or in a eutectic mixture of lithium and potassium chlorides. The cell was operated at a temperature range of 600°-900° C. under an inert atmosphere and at current densities ranging from 3-100 amps./sq. dm. Rigid controls were necessary to exclude all traces of air or moisture from the system in order to prevent the formation of lower oxides at the cathode.

ELECTRODEPOSITION FROM NON-AQUEOUS MEDIUMS

An early German patent[30] refers to a process of separating tungsten or chemically similar metals, such as chromium, molybdenum, or uranium, by electrolytic methods. It is claimed that the binary salts of these metals are soluble without decomposition or oxidation in various conducting organic liquids, such as acetone, and that electrolysis of these solutions gives a firm metal deposit.

K. Wolf[31] reports that hydrogen, molybdenum oxychloride, and sometimes metallic molybdenum are deposited from alcoholic solutions containing molybdenum chloride.

Efforts by Booth and Merlub-Sobel[32] to deposit molybdenum from liquid ammonia solutions of molybdenum pentachloride were unsuccessful; the pentachloride was relatively insoluble in the liquid ammonia. Cells were operated at -33° C. and at room temperature under a pressure of 150 p.s.i. Current density ranged from 67 - 15,200 milliamps./sq. cm.

The deposition of metals such as beryllium, tungsten, tantalum, and molybdenum from solutions of halides, nitrates, cyanides, or thiocyanates in liquid ammonia is claimed by L. St. C. Broughall.[33] The ammonia is kept in the liquid phase by either low temperature or pressure. Stainless steel and carbon may be used as electrodes.

29/ Brenner, A., and Senderoff, S., The Electrolytic Preparation of Molybdenum From Fused Salts: Jour. Electrochem. Soc., vol. 101, 1954, p. 16.

30/ Wolfram-Lampen, A. G., Electrodeposition of Tungsten or Similar Metals: German Patent 237,014, June 12, 1910.

31/ Wolf, K., /Electrochemical Behavior of Molybdenum and Some Molybdenum Compounds/: Dissert. Aachen, Tech. Hochschule, 1918, p. 38.

32/ Booth, H. S., and Merlub-Sobel, M. J., Phys. Chem., vol. 35, 1931, p. 3303.

33/ Broughall, L. St. C., Electrodeposition of Various Metals: British Patent 320,818, Dec. 31, 1938.

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CONCLUSIONS

A search of the literature on the electrodeposition of molybdenum has revealed many conflicting results obtained by different investigators. In almost no instance have investigators been able to reproduce earlier work disclosed in the literature. On the contrary, serious doubt is leveled as to the validity of many of the reported claims for the electrodeposition of molybdenum.

A review of the literature indicates that up to the present time, no satisfactory deposit of molybdenum metal has been obtained with the exception of the work reported by Brenner and Senderoff.[34/] Frequent claims in the literature concerning electrodeposition from aqueous or fused-salt systems should be carefully evaluated as the experience of many of the investigators cited indicates that only extremely thin plates, generally contaminated with lower oxides or hydroxides, are obtained.

It is probable that Brenner and Senderoff[35/] are the only investigators who have successfully obtained massive deposits of the metal. The practicability of their method from an economic standpoint has not yet been established.

The use of mercury cathodes, yielding finely divided metal powder after distillation of the mercury, does not appear promising but might allow recovery of relatively pure metal powder.

The complete exclusion of oxygen from fused-salt systems or from nonaqueous systems may be a necessary condition for obtaining massive deposits of the metal and further investigation along these lines may prove productive.

34/ See work cited in footnote 29.
35/ See work cited in footnote 29.

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